

RELATION BETWEEN HYDROCARBON STRUCTURE AND FRAGMENTS PRODUCED IN PYROLYSIS

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Analysis of the heavy molecules which form tar in hydrocarbon pyrolysis can provide clues to the mechanisms of their release and to the structure of the parent molecule. This paper considers the relationship between the original hydrocarbon structure and the product tar. Pyrolysis experiments have been performed in a heated grid apparatus on several coals and lignins and on a polymer specifically synthesized to model features of natural hydrocarbons. Tars were collected and analyzed by Fourier Transform Infrared (FT-IR) Spectroscopy. The functional group composition of tars for a bituminous coal, a lignin and a polymer are all remarkably similar to the functional group composition of the parent material. It is believed that for these samples, the tar consists of minimally disturbed fragments of the original organic matrix. Molecular weights of tars were determined by Field Ionization Mass Spectrometry (FIMS) for tars collected from the heated grid apparatus and for samples pyrolyzed directly in the FIMS apparatus. The mass spectra all exhibit features reflecting structural aspects of the parent molecule and for the softening bituminous coals, the lignin and the polymer, the upper limit of molecular weight appears limited by vaporization. The process appears to be controlled by the combined effects of pyrolysis and vaporization, where bond breaking is required to produce fragments which are small enough to volatilize. The fragments are, therefore, similar in composition to the parent solid but lower in molecular weight.

A computer model for the coupled pyrolysis and vaporization of macromolecules has been used to interpret the results. The theory combines random cleavage of weak bonds in the polymer (to produce "metaplast") with transport of depolymerization fragments by vaporization and diffusion. The theory predicts product yields and molecular weight distributions in agreement with the observed results. An attempt has also been made to fit the regular structure in the FIMS spectra with an assumed distribution of likely homologous series. Although the assignments are highly speculative, it is possible to obtain a reasonable facsimile of the FIMS spectra with chemically reasonable choices.

EXPERIMENTAL

The pyrolysis experiments were performed in an apparatus which employs an electrically heated grid within an infrared cell to provide on-line, in-situ analysis of evolved products by Fourier Transform Infrared (FT-IR) Spectrometry. In the flash pyrolysis experiments, the cell was closed and the grid was heated to a final temperature at between 600 and 2000°C/sec. Char yield was obtained gravimetrically from the residue in the grid. Tar samples were obtained from the cold glass wall of the cell or from in-line filters and yields were obtained gravimetrically. Details of the experiment have been described previously (1,2).

The field ionization mass spectrometry (FIMS) experiments were performed at SRI International. The FIMS technique ionizes molecules with minimal fragmentation and so gives a direct molecular weight distribution (3).

The preparation of the polymer, poly(1,4-dimethylenenaphthalene), naphthalene rings linked by ethylene bridges, is described elsewhere (4).

RESULTS

In relating pyrolysis products to the parent hydrocarbon, one of the most striking observations is the similarity often seen for the functional group composition of the two materials. Figure 1 shows FT-IR spectra for the tars, parent hydrocarbons and their differences for the model polymer, a lignin, a lignite, and a bituminous coal. Except for the lignite, the pairs of spectra are quite similar.

An important difference in the bituminous coal spectrum is a higher methyl group concentration in the tar which appears to result from rupture of C(aliphatic)-C(aliphatic) bonds followed by radical stabilization. Similarly the loss of C(aliphatic)-O bonds in lignin tar is probably due to rupture of ether bonds and evolution of water.

Molecular weight distributions for the heavy products obtained for these 4 samples plus two additional coals are presented in Figs. 2 and 3. All samples except for the lignin (which was pyrolyzed in the heated grid apparatus) were directly pyrolyzed in the FIMS apparatus. These samples were heated at approximately 2-3°C/min to temperatures up to 460°C. The molecular weight distribution is for the sum of products obtained during pyrolysis. The darker spectra in Figs. 2b and 3 are the odd numbered masses for molecules which include nitrogens or C¹³. The simplest spectrum is that of the polymer. It consists of oligomers from monomers to heptamers. All the oligomers are released over a narrow temperature range between 400° and 425°C. This contrasts with the results obtained when the polymer tar is used as the sample in the FIMS. In this case, the sample distills with monomers and dimers coming off below 150°C, trimers and tetramers below 275°C and pentamers and hexamers near 400°C (4). This contrast suggests that the distribution of oligomers in Fig. 2a does not result from evaporation alone, but must be controlled by pyrolysis. The next simplest spectrum is that for lignin which appears to result from monomers, dimers and trimers. The large contribution of dimers in this spectrum is thought to be due to dilignols linked by thermally stable bonds.

The mass spectra of the coal pyrolysis products (Fig. 3) are the most difficult to interpret. The spectra consist of regularly spaced clusters of peaks on top of a smooth background. The height and width of the background increases with rank. Extensive studies of coal pyrolysis products have been performed by Meuzelaar and co-workers (5-7). Their results are obtained for electron impact ionization which produces fragmentation, while the FIMS spectra presented here have negligible fragmentation. Meuzelaar's results can, however, be used to guide our assignment of many of the FIMS peaks. For example, the following homologous series have been identified in Py-MS spectra: m/z- 110, 124, 138 (dihydroxy-benzenes); m/z-94, 108, 122, 136, 150 (phenols); m/z-142, 156, 170, 184 (naphthalenes); and m/z-96, 106, 120 (benzenes).

A number of observations can be made about the spectra: 1) The peaks are organized into peak clusters which have a long range periodicity of 12 1/2 mass units. For subbituminous and higher rank coals, the peaks clusters appear to be arranged in groups of 4 with the peak clusters at 160, 210, 260, 310, etc. being larger than the previous peak cluster. The interpretation is that each set of 4 peaks is a similar series differing by an additional fused aromatic ring. After the addition of a new ring, the next peak cluster is larger by 14, representing the addition of saturated carbons, but the spacing is gradually reduced as the number of extra carbons grow, reaching 12 1/2 mass units per cluster with the addition of the next ring. The change in spacing is thought to result from increasing unsaturations as the side chains grow and form rings. 2) There are relatively low intensities at mass numbers for unsubstituted aromatics such as naphthalene and anthracene; methyl or hydroxyl substituted aromatics have higher values but bi-substituted compounds appear to achieve a maximum. The interpretation is that fragments require the breaking of at least one and, more likely, two bonds, and therefore, are left with one or more substitutions. 3) There are a number of homologous series which are separated by saturated carbons. The relationship of these peaks can be seen by plotting their intensity as a function of the time (or temperature) at which they were evolved. Fig. 4 shows a series of peaks for a Pittsburgh Seam bituminous coal at 108, 122, and 136 compared to a series at 110, 124 and 138. The latter series evolves at a shorter time (lower temperature) than the former. The interpretation is that the 110 series is dihydroxy-benzene, while the former is a methyl hydroxy-benzene. The latter will likely require the breaking of C(aliphatic)-C(aliphatic) bonds which requires more energy and have higher temperatures than the breaking of C(aliphatic) bonds. 4) The relationship between the compound class and the temperature of evolution is further examined in Fig. 4b

which presents the time-dependent intensities of 5 masses associated with one cluster for a lignite. As can be seen, the temperature of evolution goes down with increasing molecular weight. The lignite peaks are more widely separated than for the bituminous coal. As can be seen, the highest molecular weight corresponds to oxygen substituted species, while the lowest corresponds to methyl. This reduction in pyrolysis temperature of oxygenated species is consistent with the rank dependence in pyrolysis products discussed in (8) presented at this symposium. The highest and broadest profile corresponds to a molecular weight having the widest variety of contributing compounds.

DISCUSSION OF TAR FORMATION IN COAL AND OTHER HYDROCARBONS

The mechanisms of tar evolution have been considered by a number of investigations (9-16). It is generally agreed that the process includes the following steps: 1) Formation of tar molecules, 2) transport and evaporation, and 3) possible repolymerization to form coke or char. The questions are: what is the source for tar, how are tar molecules formed, what are the transport bottlenecks and what is the relationship between the formation, transport and repolymerization of tar molecules? The following conclusions were reached in a recent review (17).

1. For bituminous coals, lignins, and some polymers, tar molecules appear to be minimally disturbed fragments of the coal's organic structure. The evidence for this is the striking similarity between the tar and parent material which has been observed in elemental composition, IR spectra (see Fig. 1) and NMR spectra.

2. The production of tar molecules involves bond breaking. The possibility that tar molecules exist in the parent material and are released through evaporation without any bond breaking can be ruled out on the basis of two observations. The first is that extractable molecules generally have a higher average molecular weight than tar molecules (18-20). The second observation is that the evaporation of previously formed tar has a much different temperature dependence than evolution of tar from coal, as discussed above.

3. The variation of yield and molecular weight distribution of tar with pressure suggest that the transport is controlled by gas phase diffusion. An example of the influence of pressure on the molecular weight distribution is illustrated in Fig. 5 which presents FIMS data for a Pittsburgh Seam coal tar produced at 4 atm., and a polymer tar produced at 5 atm. The reduction of the average molecular weight with increasing pressure is striking (see Figs. 2a and 7c). Unger and Suuberg have presented similar data (11-13) and have argued (14) that for softening coals this effect and the variation of yield with pressure can be explained by assuming that the limitation is the diffusion away from the liquid surface during the evaporation process. High pressures hinder the evolution of heavier molecules leading to cracking or repolymerization.

Considering the available evidence, tar formation in softening hydrocarbons may be viewed as a combined depolymerization and evaporation process in which the pyrolytic depolymerization continually reduces the weight of the molecular fragments through bond breaking and free radical stabilization until the fragments are small enough to be evaporated.

For non-softening coals, vaporization at the ambient pressure of the experiment does not appear to be the transport bottleneck. In Figs. 2 and 3, the very low molecular weight of the tars from non-softening lignite and subbituminous coal compared to that from the softening polymer, lignin and bituminous coal, suggests that some other mechanism for limiting the evolution of high molecular weight components must exist, possibly activated diffusion in the solid as suggested by Gavalas et al (15).

MODELING

A theory for the combined effects of bond breaking and vaporization has been developed. The theory combines random cleavage of weak bonds (similar to the concept used by Gavalas et al (15)) with transport of depolymerization fragments by vaporization and diffusion (like Unger and Suuberg (14)) to predict product yield

and composition. The assumptions in this theory include: (1) the bonds between the monomer units in the polymer molecules are the only weak bonds and are equally likely to be cleaved; and (2) repolymerization to form a different chemical structure is not included.

For any oligomer (1) with molecular weight M_1 the theory computes the rate of loss due to bond breaking to form smaller oligomers, the rate of increase due to formation of new oligomers from the breaking of higher molecular weight oligomers and the rate of loss due to evaporation. The process continues as long as hydrogen is available to stabilize the free radicals. Integrating the rate equations over time yields the amount and molecular weight distribution of the vaporized products which constitutes the tar. The computations for the polymer (which has only one monomer) are the numbers in parenthesis on Figs. 2 and 5. The predictions compare favorably with the second set of numbers which are the observed integrated intensities. The theory applied to lignin assuming 7 monomers was described in a recent publication (21). The theory gives reasonable results.

Coal is more difficult to model because of the variety of monomer types and bond energies. We have attempted to get a monomer distribution by fitting the clusters of peaks which show up consistently in the FIMS spectra. The scheme is outlined in Fig. 6. Starting with three basic single ring compounds with the probability for occurrence listed in column A, side chains (or 5 membered rings) are added with the probabilities in column B. Additional fused aromatic rings are added with the probabilities in column C and additional hydrogens to saturate the rings are added in column D. The probabilities shown are for the Pittsburgh Seam coal FIMS in Fig. 7c. The distribution of all possible combinations (the monomer distribution) is illustrated in Fig. 7a which compares reasonably well with the peak clusters in Fig. 7c. The dimer distribution is obtained by adding this distribution (minus 2 to account for the loss of hydrogen in the dimer bridge) to a second monomer distribution which includes molecular weights below 100 (introduced artificially by taking off one fused ring). The dimers were added to the monomers in a ratio of 3:1. This is a departure from the above theory which predicts that initially all oligomers are equally likely, but this compensates for the lack of trimers and tetramers. The resulting distribution is then convoluted with a vaporization probability to produce Fig. 7b which now has the peak clusters as well as the smooth background. The exercise shows that the assumed simple distribution is a possible choice. Other possibilities may also fit, but the choice must have sufficient regularities to produce the observed FIMS peaks.

The lignite molecular weight distribution is clearly controlled by processes other than vaporization as indicated by the lack of appreciable molecules above 200. Lignite is a non-softening solid. The rigid cross-linked nature of the molecular structure provides several possible explanations: (1) the cross-link density is so high and the available hydrogen for stabilization so low that there are very few dimers and trimers which can be released; (2) the rigid structure sterically hinders the escape of large molecules; (3) the rigid structure creates high pressures in the pores which hinders the escape of large molecules. These possibilities are currently under investigation.

CONCLUSIONS

1. Pyrolysis tars for a number of different hydrocarbons including softening coal, lignin and model polymers appear to be minimally disturbed fragments from the parent hydrocarbons. 2. FIMS spectra are useful in providing unfragmented molecular weight distributions for tar. The spectra for coals are remarkably regular. All spectra have the same series of peak clusters. Rank variations show up as variations in the intensity of the peak clusters and in the amount and width of a smooth background. 3. The spectra of the simplest compounds (lignin and a model polymer) can be modeled by a theory which combines random cleavage of weak bonds to form oligomers which are small enough to vaporize. The theory predicts the correct trends for softening coals but not for lignite and low rank coals. 4. A speculative scheme for matching FIMS spectra of coals with an assumed monomer distribution appears to give reasonable results.

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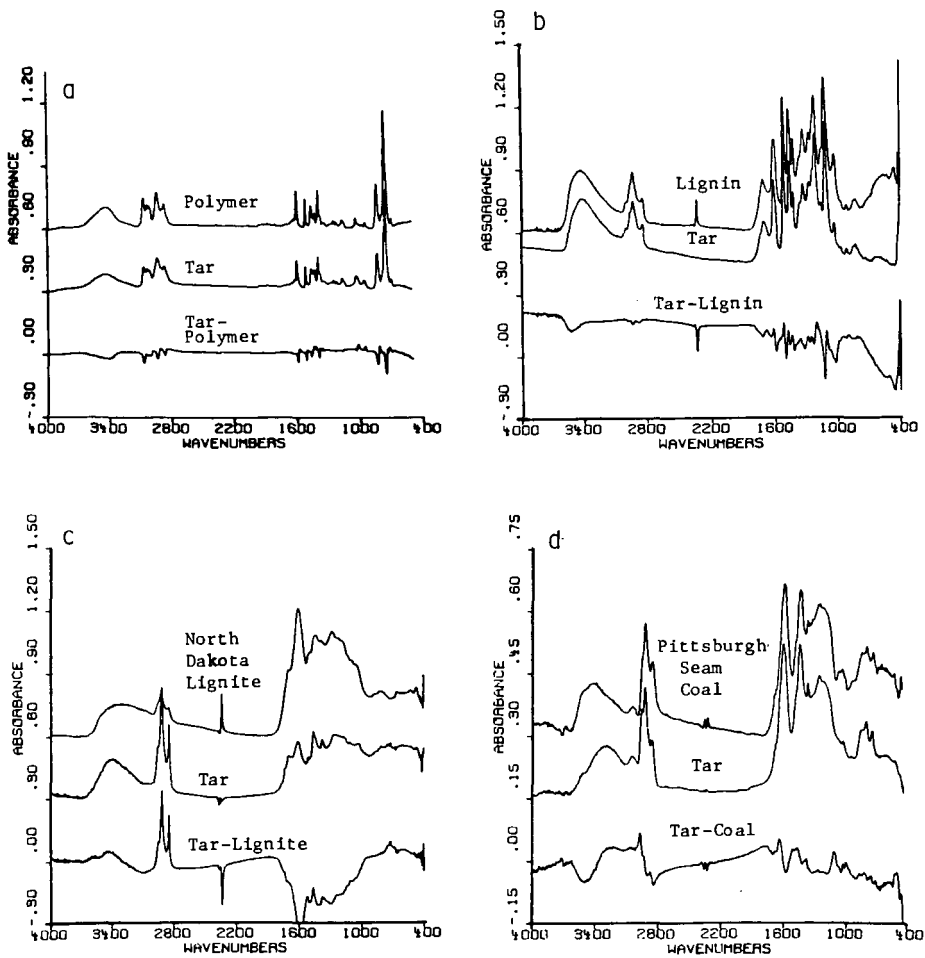


Figure 1. Comparison of FT-IR Spectra of Hydrocarbons and their Pyrolysis Tars.

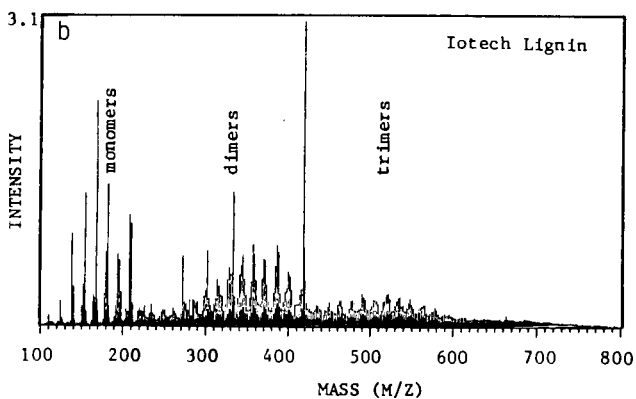
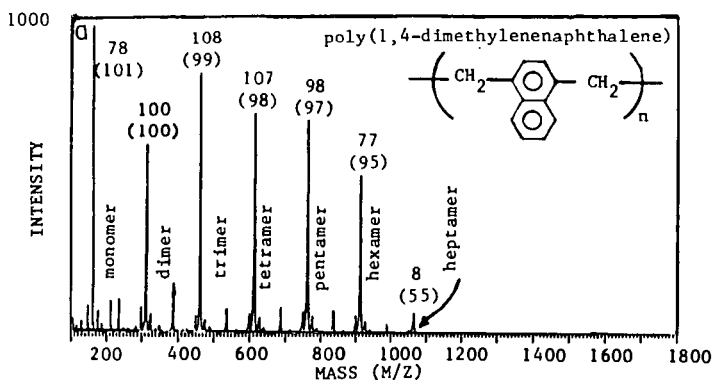


Figure 2. FIMS Spectra of two Hydrocarbons.

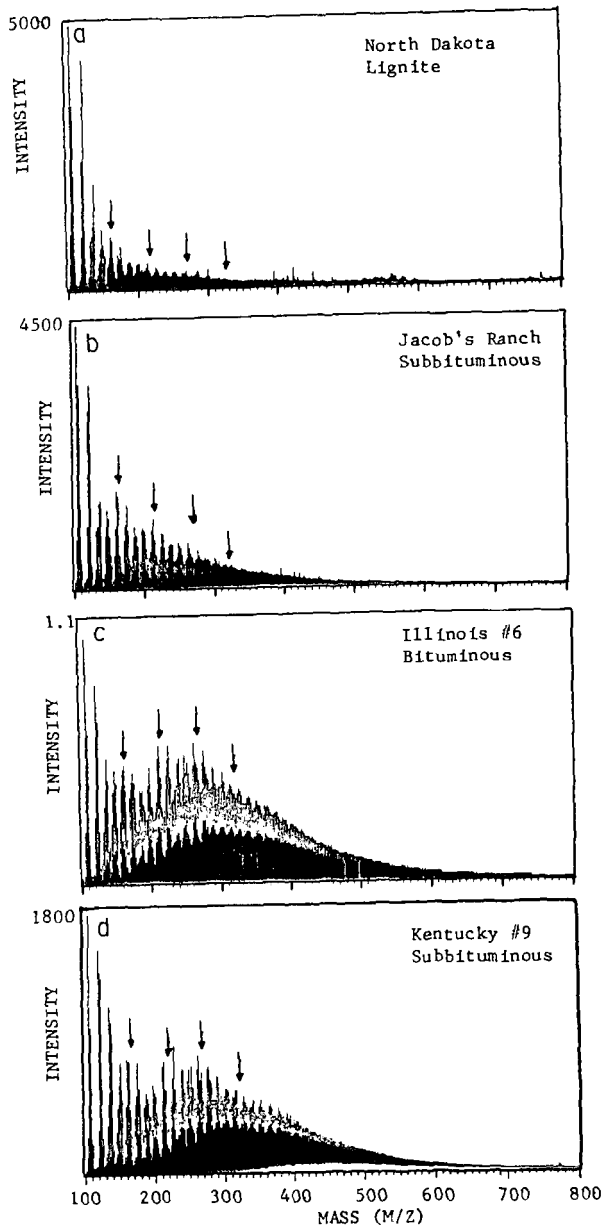


Figure 3. FIMS Spectra of a Lignite and 3 Coals. Arrows designate larger Peaks which begin Series of 4 Peak Clusters.

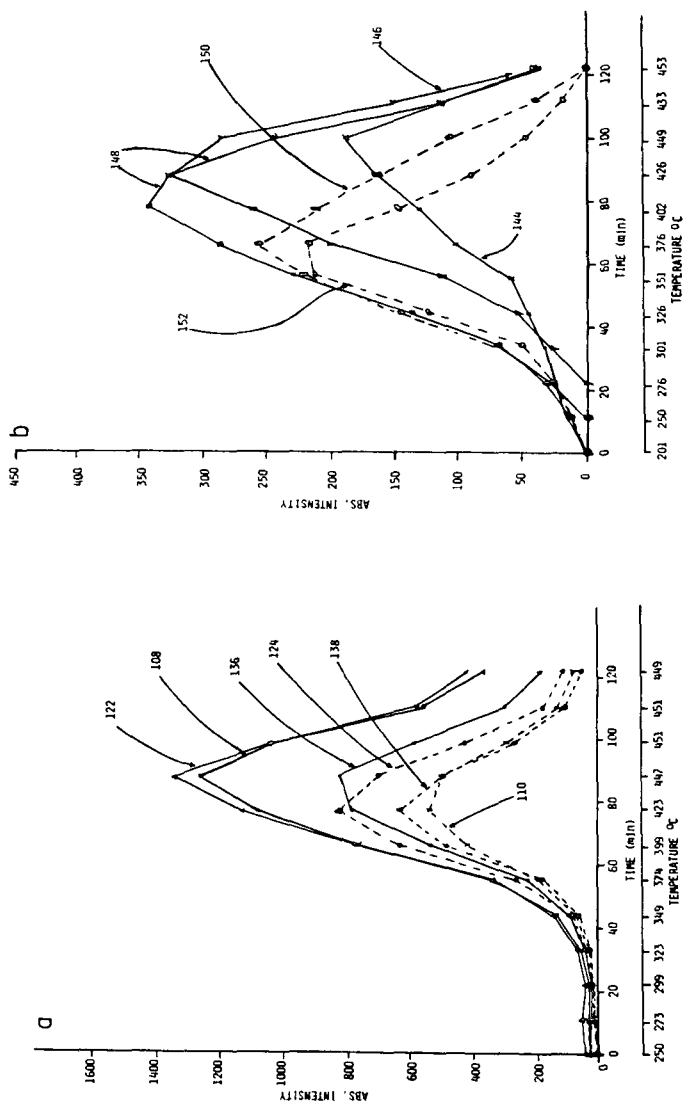


Figure 4. Intensity of Individual Mass Peaks as a Function of Pyrolysis Temperature.

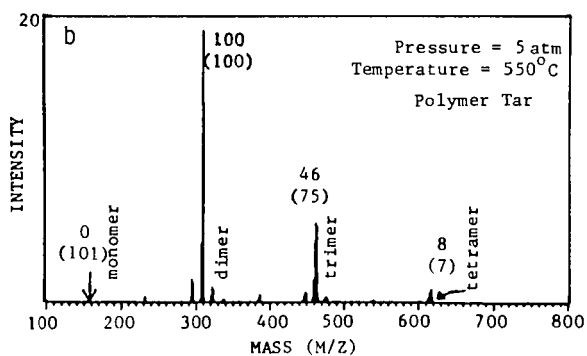
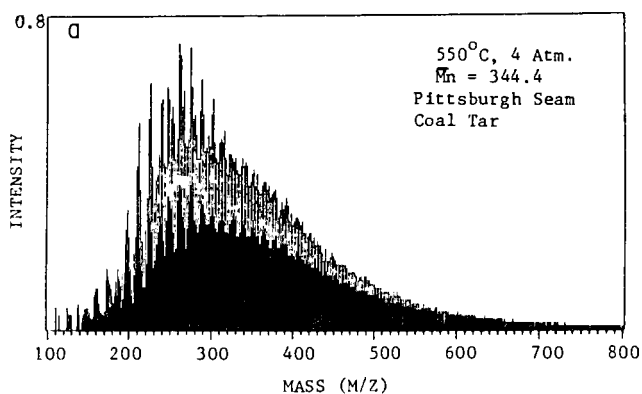


Figure 5. FIMS Spectra of two Hydrocarbon Tars Produced at Elevated Pressure. Spectra for Tars from the same Hydrocarbon produced in Vacuum are presented in Figs. 2a and 7c.




a			b			c			d		
BASIC COMPOUND			SIDE GROUPS			ADDITIONAL FUSED RINGS			RING SATURATION		
MW	Compound	Probability	MW	Group	Probability	MW	Number of Rings	Probability	MW	Number of Hydrogens	Probability
106		0.2	0	-	1.0	0	-	1.0	0	0	.25
			12	C	0.1	50	1	.6	2	2	.25
			14	CH ₂	1.0	100	2	.6	4	4	.5
108		1.0	24	C ₂	0.1	150	3	.6	6	6	.25
			26	C ₂ H ₂	0.2	200	4	.3	10	10	.25
			28	C ₂ H ₄	0.5	250	5	.2			
110		0.3	36-42	C-C ₂ H ₆	0.25	300	6	.1			
			48-56	C ₄ -C ₄ H ₈	0.15						
			60-70	C ₅ -C ₅ H ₁₀	0.07						

Figure 6. Compounds and Probabilities for Monomer Distribution in a Pittsburgh Seam Coal.

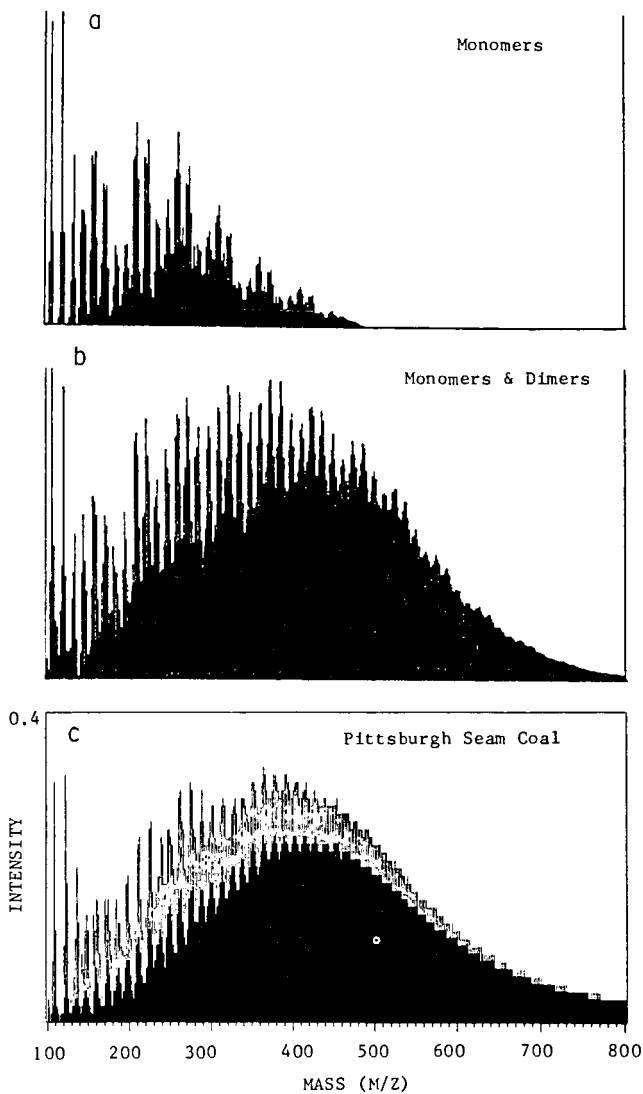


Figure 7. FIMS Spectra for a Pittsburgh Seam Coal (c) and Synthesized Spectra for Monomers and Monomers Plus Dimers.